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(54) AMINOARYLOXY-ARYLCARBOXYLIC ACID NITRILES AND A PROCESS FOR THEIR PREPARATION

(71) We, BAYER AKTIENGESELLSCHAFT, formerly known as Farbenfabriken Bayer Aktiengesellschaft, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to aminoaryloxy-arylcarboxylic acid nitriles and to a process for their preparation. In particular, the invention relates to aminoaryloxy-arylcarboxylic acid nitriles and a process for their preparation which comprises reacting a 2-halo or 4-halo or nitro-benzonitrile with an alkali metal salt of an aminophenol in a polar, aprotic solvent and in the absence of water.

The conventional methods described in the literature for the preparation of phenoxy-benzonitriles consist of melting anhydrous potassium phenolate with 2- or 4-bromo-benzonitrile with the result that potassium bromide is split off and 2- or 4 - phenoxy - benzonitrile is obtained in low yields. The nitrile group may also be introduced by the Sandmeyer reaction by diazotising suitable aromatic aminophenoxy compounds and reacting them with cyanides.

In German Offenlegungsschrift No. 1,912,600 it has been disclosed that the alkali metal salts of unsubstituted phenols or of phenols substituted with halogen or alkyl groups react with 4-chlorobenzonitrile in dimethylformamide or dimethylsulphoxide solution to yield para - aryloxy - benzonitriles with elimination of alkali metal chloride.

Further, it has been disclosed in German Offenlegungsschrift No. 1,593,871 that alkali metal aminophenolates can be selectively reacted on the phenol group with reactive aromatic halogen compounds such as ortho- or para-chloronitrobenzene to yield aminophenoxynitrobenzenes. This reaction, however, provides high yields of the above mentioned compounds only if it is carried out in polar, aprotic solvents under mild conditions, *i.e.* only moderately elevated temperatures, because at higher temperatures the amino group, which is also reactive, enters into the reaction. As is well known, moreover, aminophenols are very liable to undergo oxidation, especially in a basic medium, to give rise to coloured decomposition products.

It was therefore surprising that when aromatic halo- and nitro-carboxylic acid nitriles in which the halogen atom or nitro group is in the ortho-position or para-position to the nitrile function are subjected to nucleophilic substitution with alkali metal amino phenolates in polar, aprotic solvents at elevated temperature, the reaction takes place selectively, the free amino group is obtained, and high yields of amino - aryloxy - arylcarboxylic acid nitriles result.

These compounds cannot be synthesised directly by the process conventionally used in the art.

The present invention provides a process for the preparation of a substituted aryl ether, wherein an aminophenol having the following general formula (I):

$$H_2N—Ar^1—OH \qquad (I)$$

wherein

Ar^1 represents an aromatic ring system with from 6 to 14 carbon atoms which may be unsubstituted or substituted with halogen, alkyl, amino or carboxyl groups

is reacted with a stoichiometric quantity of an alkali metal hydroxide or alkali metal alcoholate and the resulting anhydrous alkali metal aminophenolate is reacted with an arylcarboxylic acid nitrile of the following general formula (II):

[*Price 25p*]

$$\mathrm{Hal—Ar^2—(CN)_x} \quad \text{(II)}$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad (R)_y$$

wherein

Hal represents chlorine or bromine which is in the ortho- or para-position to at least one nitrile group,

Ar^2 represents an optionally substituted aromatic ring system with from 6 to 14 carbon atoms,

R represents halogen, an alkyl, alkoxy, alkylthio, acyl, alkylsulphonic or arylsulphonic acid group or a nitro group which is not in the ortho- or para-position to a nitrile group,

x represents the integer 1 or 2, and

y represents the integer 1, 2 or 3,

or with an arylcarboxylic acid nitrile of the following general formula (III):

$$\mathrm{O_2N—Ar^2\ (CN)_x} \quad \text{(III)}$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad (R)_y$$

wherein

NO_2 is in the ortho- or para-position to at least one nitrile group,

Ar^2, x and y are as just defined, and

R denotes halogen, an alkyl, alkoxy, alkylthio, acyl, alkylsulphonic or arylsulphonic acid group or a nitro group,

in a polar aprotic solvent at an elevated temperature, optionally in an inert gas atmosphere.

The following are mentioned as examples of suitable aminophenols for the purpose of the invention:

2-Aminophenol, 3-aminophenol, 4-aminophenol, 3 - amino - *p* - cresol, 2,4-diaminophenol, 3 - chloro - 4 - aminophenol, 4 - chloro - 2 - aminophenol, 3 - amino - 4 - hydroxybenzoic acid, 5 - amino - 1 - naphthol, 6 - amino 1 - naphthol and 7 - amino - 2 - naphthol.

Suitable aromatic halo- or nitro-carboxylic acid nitriles are those in which the nucleophilic exchange between the halogen or nitro group and the aminophenolate ion is enabled to take place by at least one activating nitrile group in the ortho- or para-position. The substituents may be any atoms or groups which are inert under the conditions of condensation. The following are examples of acrylcarboxylic acid nitriles which may be used in the process of the invention:

2 - Chloro - benzonitrile, 4 - chloro - benzonitrile, 3,4 - dichloro - benzonitrile, 4 - chloro - 2 - nitro - benzonitrile, 2 - chloro - 4 - nitro - benzonitrile, 4 - chloro - phthalic acid dinitrile, 4 - chloro - isophthalic acid dinitrile, nitro-terephthalic acid dinitrile, 2 - methyl - 4 - chloro - benzonitrile, 2 - methyl - 4,5 - dichloro - benzonitrile, 2 - chloro - 4 - ethyl - thiobenzonitrile, 2 - chloro - 5 - phenylsulphonyl - benzonitrile, 4 - chloro - 1 - naphthoic acid nitrile, 4 - chloro - anthraquinone - 2 - carboxylic acid nitrile, 2 - chloro - anthraquinone - 3 - carboxylic acid nitrile and 1 - chloro - anthraquinone - 4 - carboxylic acid nitrile.

Suitable polar, aprotic solvents are *e.g.* dimethyl formamide, dimethylacetamide, N - methyl - caprolactam, N - methyl - pyrrolidone, tetramethylurea, tetramethylenesulphone, hexamethylphosphoric acid triamide and especially dimethylsulphoxide. The anhydrous aminophenolates are prepared by dissolving aminophenol in the polar solvent, preferably under a protective gas atmosphere, producing the aminophenolate by the addition of an equivalent quantity of an alkali metal hydroxide or alcoholate in the solid or dissolved form, and dehydrating the solution by azeotropic dehydration with the aid of a dragging agent or by "partial distillation".

The arylcarboxylic acid nitrile is added either in the solid form or as a solution to the resulting solution or suspension of anhydrous aminophenolate and condensation is preferably carried out at a temperature of from 20°C to 180°C., more preferably 20°C. to 130°C., for 2 to 8 hours until completed. Isolation of the aminoaryloxy-arylcarboxylic acid nitriles prepared according to the invention is advantageously carried out by the concentrating the reaction mixture by distilling off a major part of the solvent and then depositing the reaction produce in a crystalline or oily form by the addition of water or alcohol/water mixtures. The crude products may be purified in the usual manner by recrystallisation or vacuum distillation.

This invention also relates to aminoaryloxy-arylcarboxylic acid nitriles of the following general formula (IV):

$$\mathrm{H_2N—Ar^1—O—Ar^2—(CN)_x}$$
$$\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\quad (R)_y$$

wherein

Ar^2 represents an optionally substituted aromatic ring system with from 6 to 14 carbon atoms,

R represents halogen, an alkyl, alkoxy, alkylthio, acyl, alkylsulphonic or arylsulphonic acid group or a nitro group which is not in the ortho- or para-position to a nitrile group and with the proviso that at least one nitrile group is in the ortho- or para-position to the ether oxygen,

x represents the integer 1 or 2,

y represents the integer 1, 2 or 3 and

Ar^1 represents an aromatic ring system

with from 6 to 14 carbon atoms which is unsubstituted or substituted with at least one halogen, alkyl, amino or carboxyl group.

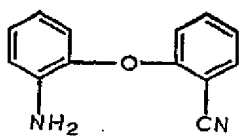
Most of the aminoaryloxy-arylcarboxylic acid nitriles prepared according to the invention have not previously been described in the literature. They are valuable intermediate products for chemical syntheses, especially for catalytic hydrogenation to produce aromatic-aliphatic diamines which are important products in the field of plastics and fibres. Other chemical conversions of aminoaryloxy-arylcarboxylic acid nitriles lead to physiologically active substances which may have important applications in agriculture.

The following Examples further illustrate the invention. Parts by weight are related to parts by volume as kilogram are to litre.

Example 1

109 Parts by weight of 2-aminophenol are dissolved in 500 parts by volume of dimethylsulphoxide, a concentrated aqueous solution of 68 parts by weight of 86% potassium hydroxide and 300 parts by volume of toluene are added in a stream of nitrogen and the reaction mixture is boiled under reflux in a water separator until no more water separates. The toluene is then evaporated off under vacuum, 150 parts by weight of 2-chlorobenzonitrile are added at 80°C. and the reaction mixture is heated to 120°C. and stirred in a stream of nitrogen at from 120°C. to 130°C. for 6 hours.

About 350 parts by volume of dimethylsulphoxide are distilled off under vacuum. The residue is poured into 1000 parts by volume of water. The products, which is deposited in the form of an oil, is dissolved in dioxane and the solution is dehydrated with anhydrous sodium sulphate, filtered through active charcoal and distilled under vacuum. 130 Parts by weight, corresponding to 62% of the theoretical yield based on the amount of 2-aminophenol used, of the following compound



are obtained in the form of an oil, b.p. 178 to 183°C./0.6 mm. Hg. The compound forms a picrate which has a melting point of 143°C. to 150°C.

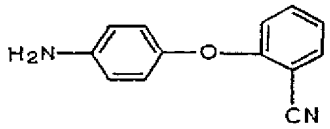
Analysis:

$C_{13}H_{10}N_2O \cdot C_6H_3N_3O_7$ (picrate)=439.3

	C	H	N
Calculated:	52.0%	3.0%	15.9%
Found:	51.9%	3.3%	16.0%

Example 2

A concentrated aqueous solution of 68 parts by weight of 86% potassium hydroxide is added to a solution of 109 parts by weight of 4-aminophenol in 1000 parts by volume of dimethylsulphoxide and the solution is dehydrated by vacuum distillation of about 300 parts by volume of a mixture of dimethylsulphoxide and water. 150 Parts by weight of 2-chlorobenzonitrile are added and the reaction mixture is stirred in a stream of nitrogen at from 120°C. to 130°C. for 6 hours. After cooling to room temperature, the reaction product is precipitated with water, filtered through a suction filter and washed with water. The dry crude product (190 parts by weight, melting point 115°C. to 119°C.) is purified by recrystallisation from ethanol. The yield obtained is 153.2 parts by weight, corresponding to 73% of the theoretical yield based on the amount of 4-aminophenol used, of the following compound:



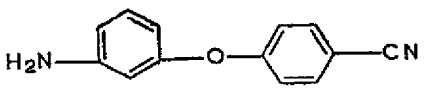
which has a melting point in the range of 119 to 121°C.

Analysis: $C_{13}H_{10}N_2O$=210.2

	C	H	N
Calculated:	74.3%	4.80%	13.30%
Found:	74.5%	5.20%	13.00%

Example 3

Sodium - 3 - aminophenolate prepared from 109 parts by weight of 3-aminophenol and a freshly prepared methyl alcoholic solution of 54 parts by weight of sodium methylate in 500 parts by volume of dimethylsulphoxide is free from methanol by partial distillation. After addition of 145 parts by weight of 4-chlorobenzonitrile, the mixture is stirred under nitrogen at 130°C. for 5 hours. 250 parts by volume of dimethylsulphoxide are distilled off under vacuum. The reaction product in the distillation residue is precipitated by dropwise addition of water after the addition of methanol. The product is removed by suction filtration, washed with water and crystallised from ethanol. After isolation of the product and drying, 141 parts by weight, corresponding to 67% of the theoretical yield based on the amount of 3-aminophenol used, of the following compound:



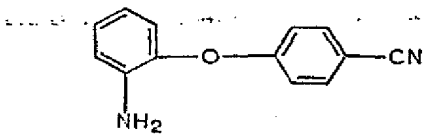
which has a melting point of 86 to 88°C. are obtained.

Analysis: $C_{13}H_{10}N_2O$=210.2

	C	H	N
Calculated:	74.3%	4.80%	13.30%
Found:	74.3%	4.80%	12.90%

Example 4

The aminophenolate prepared from 109 parts by weight of 2-aminophenol and 54 parts by weight of sodium methylate is reacted with 145 parts by weight of 4-chlorobenzonitrile and worked up as described in Example 3. Using a procedure exactly analogous to that described in Example 3, the yield obtained is 151.5 parts by weight=72% of the theoretical yield based on the amount of 2-aminophenol used, of the following compound:



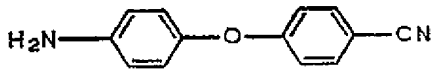
which has a melting point of 123 to 125°C.

Analysis: $C_{13}H_{10}N_2O$=210.2

	C	H	N
Calculated:	74.3%	4.80%	13.30%
Found:	74.0%	4.90%	12.80%

Example 5

The dimethylsulphoxide solution of sodium - 4 - aminophenolate prepared from 218 parts by weight of 4-aminophenol and the equivalent quantity of sodium methylate as described in Example 3 is reacted with 290 parts by weight of 4-chlorobenzonitrile at 130°C. for 5 hours as also described above. 315.7 Parts by weight or 75.3% of the theoretical amount, based on the amount of 4-aminophenol used, of the following compound:



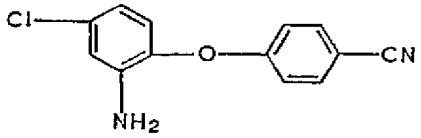
which has a melting point of 110 to 111°C. are obtained after isolation and recrystallisation as described above.

Analysis: $C_{13}H_{10}N_2O$=210.2

	C	H	N
Calculated:	74.3%	4.8%	13.3%
Found:	74.0%	5.0%	13.1%

Example 6

143.5 Parts by weight of 4 - chloro - 2 - aminophenol are reacted with 145 parts by weight of 4 - chloro - benzonitrile by a procedure analogous to that described in Example 3. The crude product is recrystallised three times from ethanol. 89.4 Parts by weight or 36.8% of the theoretical amount based on the amount of 4 - chloro - 2 - aminophenol used, of the following compound:



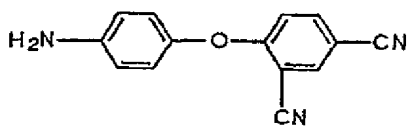
which has a melting point of 122 to 123°C. are obtained.

Analysis: $C_{13}H_9ClN_2O$=244.7

	C	H	N	O	Cl
Calculated:	63.8%	3.7%	11.45%	6.55%	14.5%
Found:	63.9%	3.8%	11.30%	6.70%	14.5%

Example 7

32.7 Parts by weight of 4-aminophenol are dissolved in 300 parts by volume of dimethylsulphoxide, and a concentrated aqueous solution of 19.5 parts by weight of 86% potassium hydroxide is added. The reaction product is dehydrated by distilling off about 100 parts by volume of solvent mixture under vacuum. A solution of 49 parts by weight of 4-chloroisophthalic acid dintrile in 150 parts by volume of dimethylsulphoxide is added dropwise at 35°C. to 60°C. The reaction mixture is stirred under nitrogen at 60°C. to 70°C. for 3 hours, 200 parts by volume of dimethylsulphoxide are removed by vacuum distillation, and the reaction product is precipitated by stirring 200 parts by volume of water into it. The product is separated by suction filtration, washed with water and purified by recrystallisation from acetonitrile. 58.3 Parts by weight or 82.7% of the theoretical yield of the following compound:



which has a melting point of 189 to 190°C. are obtained.

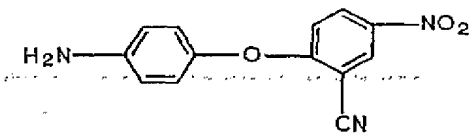
Analysis: $C_{14}H_9N_3O$=235.2

	C	H	N	O
Calculated:	71.5%	3.85%	17.85%	6.8%
Found:	71.0%	3.90%	17.90%	7.8%

Example 8

A sodium methylate solution freshly prepared from 23 parts by weight of sodium is added to 109 parts by weight of 4-amino-

phenol in 500 parts by volume of dimethylsulphoxide. The methanol is removed by partial distillation, and a solution of 185 by weight of 2 - chloro - 5 - nitrobenzonitrile in 300 parts by volume of dimethylsulphoxide are run in at 40°C. to 50°C. while the solution is being cooled. After stirring under nitrogen for 4 hours at 60°C. to 70°C., the product is precipitated with water after the addition of methanol. The crude product is removed by suction filtration, washed with water and recrystallised moist from a mixture of dioxane, water and methanol. 199 Parts by weight or 78% of the theoretical yield, based on the amount of 4-aminophenol used, of the following compound:



which has a melting point of 166 to 168°C. are obtained.

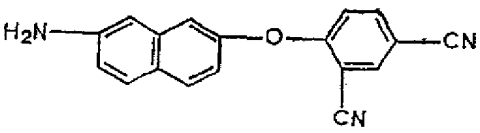
A sample removed for analysis is found to have a melting point of 168 to 168.5°C. after recrystallisation from a mixture of dioxane and water.

Analysis: $C_{13}H_9N_3O_3$=255.2

	C	H	N	O
Calculated:	61.2%	3.56%	16.45%	18.8%
Found:	60.2%	3.80%	16.40%	19.2%

Example 9

39 Parts by weight of 2 - hydroxy - 7 - amino - naphthalene hydrochloride are dissolved in 200 parts by weight of dimethylsulphoxide, and the concentrated aqueous solution of 26 parts by weight of 86% potassium hydroxide is added. After removal of 100 parts by volume of dimethylsulphoxide by distillation, a solution of 33.5 parts by weight of 4 - chloro - isophthalic acid dinitrile in 100 parts by volume of dimethylsulphoxide is added at 50°C. to 60°C. with slight cooling. The reaction mixture is stirred under nitrogen for 3 hours at 70°C. and the reaction product is precipitated by the addition of water. After suction filtration, washing and recrystallisation from acetonitrile, 42.4 parts by weight or 74.3% of the theoretical yield, based on the amount of 2 - hydroxy - 7 - amino - naphthalene hydrochloride used, of the following compound:



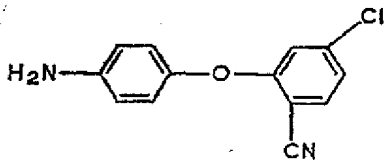
which has a melting point of 174—175°C. are obtained.

Analysis: $C_{18}H_{11}N_3O$=285.3

	C	H	N	O
Calculated:	75.8%	3.9%	14.7%	5.6%
Found:	75.4%	3.8%	15.3%	6.0%

Example 10

A mixture of 109 parts by weight of 4-aminophenol, 600 parts by volume of dimethylsulphoxide and a concentrated aqueous solution of 65 parts by weight of 86% potassium hydroxide is dehydrated by partial distillation. A solution of 188.5 parts by weight of 4 - chloro - 2 - nitro - benzonitrile in 250 parts by volume of dimethylsulphoxide is added dropwise at 50°C. to 60°C. with cooling. After stirring under nitrogen for 3 hours at 60°C. to 70°C., about 450 parts by volume of dimethyl-sulphoxide are distilled off under vacuum. The product is precipitated from the distillation residue by slowly adding 400 parts by volume of water dropwise after the addition of 50 parts by volume of methanol. The crude product is removed by suction filtration, washed with water and recrystallised moist from ethanol. 161.5 Parts by weight or 66.0% of the theoretical yield, based on the amount of 4-aminophenol used, of the following compound:



which has a melting point of 123 to 124°C. are obtained.

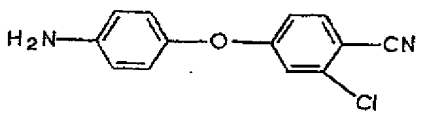
Analysis: $C_{13}H_9ClN_2O$=244.7

	C	H	Cl	N
Calculated:	63.85%	3.7%	14.5%	11.42%
Found:	63.40%	3.6%	14.2%	11.80%

Example 11

109 Parts by weight of 4-aminophenol are converted into the sodium salt as described in Example 3. A solution of 182.5 parts by weight of 2 - chloro - 4 - nitro - benzonitrile in 300 parts by volume of dimethylsulphoxide is gradually poured into the resulting suspension at 50°C. to 60°C. The mixture is stirred under nitrogen for 6 hours at 70°C., most of the solvent is removed by vacuum distillation, and the reaction product is precipitated by slowly adding water dropwise at room temperature after the addition of methanol. After suction filtration, washing with water and recrystallisation from

methanol, 174 parts by weight or 71% of the theoretical amount of the following compound:



which has a melting point of 120 to 122°C. are obtained.

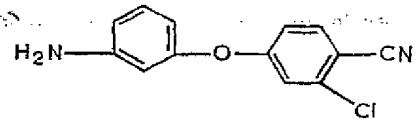
A sample removed for analysis has a melting point of 122°C. to 123°C. after recrystallisation from methanol.

Analysis: $C_{13}H_9ClN_2O$=244.7

	C	H	Cl	N
Calculated:	63.85%	3.7%	14.5%	11.42%
Found:	64.00%	4.0%	14.5%	11.50%

Example 12

A solution of 365 parts by weight of 2 - chloro - 4 - nitrobenzonitrile in dimethylsulphoxide is added at 50°C. to the anhydrous potassium salt prepared from 218 parts by weight of 3-aminophenol and 132 parts by weight of 86% potassium hydroxide by partial distillation of the dimethylsulphoxide solution. The reaction mixture is stirred under nitrogen for 4 hours at 80°C. and cooled and the product is precipitated with water after the addition of methanol. The crude product is isolated by suction filtration, washed with water and recrystallised from a mixture of ethanol and water. 359 Parts by weight or 73.5% of the theoretical yield of the following compound:



which has a melting point of 80 to 83°C. are obtained.

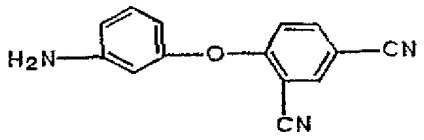
A sample removed for analysis is again recrystallised from ethanol and is then found to have a melting point of 85 to 87°C.

Analysis: $C_{13}H_9ClN_2O$=2.447

	C	H	Cl	N
Calculated:	63.85%	3.7%	14.5%	11.42%
Found:	63.80%	3.8%	14.5%	11.10%

Example 13

162.5 Parts by weight of solid 4 - chloro - isophthalic acid dinitrile are added to the dehydrated dimethylsulphoxide solution of the salt obtained from 109 parts by weight of 3 - amino - phenol and 66 g. of 86% potassium hydroxide at 60°C. and the reaction mixture is stirred under nitrogen for 4 hours at 80°C. After the addition of ethanol, the condensation product is precipitated with ice water and then recrystallised twice from a mixture of ethanol, dioxane and water after suction filtration and washing. 105 parts by weight or 45% of the theoretical amount of the following compound:



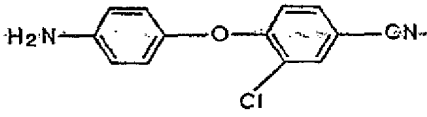
which has a melting point of 149 to 150°C. are obtained.

Analysis: $C_{14}H_9N_3O$=235.2

	C	H	N	O
Calculated:	71.5%	3.85%	17.85%	6.8%
Found:	71.4%	3.70%	17.60%	6.9%

Example 14

An anhydrous dimethylsulphoxide solution of the potassium salt obtained from 109 parts by weight of 4-aminophenol and 66 parts by weight of 86% potassium hydroxide and a dimethyl sulphoxide solution of 172 parts by weight of 3,4-dichlorobenzonitrile are stirred together under nitrogen for 4 hours at 50°C. The reaction product is precipitated with ice water after the addition of methanol and filtered through a suction filter. After recrystallisation from ethanol, 183 parts by weight or 74.8% of the theoretical amount of the following compound:



which has a melting point of 110 to 111°C. are obtained.

Analysis: $C_{13}H_9ClN_2O$=244.7

	C	H	N	O	Cl
Calculated:	63.8%	3.7%	11.45%	6.55%	14.5%
Found:	63.8%	3.7%	11.20%	6.50%	14.6%

WHAT WE CLAIM IS:—

1. A process for the preparation of a substituted arylether, in which an aminophenol of the following general formula (I):

$$H_2N—Ar^1—OH \qquad (I)$$

wherein

Ar^1 represents an aromatic ring system

having from 6 to 14 carbon atoms which is unsubstituted or substituted with at least one halogen, alkyl, amino or carboxyl group

is reacted with a stoichiometric quantity of an alkali metal hydroxide or an alkali metal alcoholate, and the resulting anhydrous alkali metal aminophenolate is reacted with an aryl carboxylic acid nitrile of the following general formula (II):

$$\mathrm{Hal—Ar^2(R)_y—(CN)_x} \qquad \text{(II)}$$

wherein

Hal represents chlorine or bromine which is in the ortho- or para-position to at least one nitrile group,

Ar^2 represents an optionally substituted aromatic ring system with from 6 to 14 carbon atoms,

R represents halogen, an alkyl, alkoxy, alkylthio, acyl, alkylsulphonic or arylsulphonic acid group or a nitro group which is not in the ortho- or para-position to a nitrile group,

x represents 1 or 2, and

y represents 1, 2 or 3,

or with an acrylcarboxylic acid nitrile of the following general formula (III):

$$\mathrm{O_2N—Ar^2(R)_y—(CN)_x} \qquad \text{(III)}$$

wherein

NO_2 is in the ortho- or para-position to at least one nitrile group,

Ar^2, x and y are as just defined, and

R represents halogen or an alkyl, alkoxy, alkylthio, acyl, alkylsulphonic, alkylsulphonic acid or a nitro group.

in a polar, aprotic solvent at an elevated temperature.

2. A process as claimed in claim 1, wherein the reaction takes place in an inert gas atmosphere.

3. A process as claimed in claim 2, wherein the reaction takes place in an atmosphere of nitrogen.

4. A process as claimed in any of claims 1 to 3, wherein the polar, aprotic solvent is dimethylsulphoxide.

5. A process as claimed in any of claims 1 to 4, wherein the arylcarboxylic acid nitrile is added in the solid form or as a solution to the resulting solution or suspension of the anhydrous aminophenolate.

6. A process as claimed in any of claims 1 to 5, wherein the arylcarboxylic acid nitrile is reacted with the anhydrous aminophenolate at a temperature of from 20°C. to 180°C. for from 2 to 8 hours.

7. A process as claimed in claim 6, wherein the arylcarboxylic acid nitrile is reacted with the anhydrous aminophenolate at a temperature of from 20°C. to 130°C.

8. A process as claimed in claim 1, substantially as herein described with reference to any of the specific Examples.

9. A substituted arylether when prepared by a process as claimed in any claims 1 to 8.

10. Aminoaryloxy - arylcarboxylic acid nitriles of the following general formula (IV):

$$\mathrm{H_2N—Ar^1—O—Ar^2(R)_y—(CN)_x} \qquad \text{(IV)}$$

wherein

Ar^2 represents an optionally substituted aromatic ring system with from 6 to 14 carbon atoms,

R represents halogen, an alkyl, alkoxy, alkylthio, acyl, alkylsulphonic or arylsulphonic acid group or a nitro group which is not in the ortho- or para-position to a nitrile group and with the proviso that at least one nitrile group is in the ortho- or para-position to the ether oxygen,

x represents the integer 1 or 2,

y represents the integer 1, 2 or 3 and

Ar^1 represents an aromatic ring system with from 6 to 14 carbon atoms which is unsubstituted or substituted with at least one halogen, alkyl, amino or carboxyl group.

11. Aminoaryloxy - arylcarboxylic acid nitriles as claimed in claim 10, substantially as herein described with reference to any of the specific Examples.

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